A SURVEY OF THERMAL DECOMPOSITION OF SOLID INSULATIONS AND ITS RELEVANCE TO BREAKDOWN MECHANISMS IN PARTIAL VACUUM

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Abstract

Several practical issues must be considered when solid electrical insulation is used in a low pressure environment. While the low pressure environment or partial vacuum (in this context, a region which is almost devoid of any gaseous media) can exhibit good electrical insulating properties, the materials contained within the partial vacuum will effect the insulation integrity over time. Degradation of the insulating properties of the partial vacuum may be due to outgassing of enclosed materials and/or adverse media contained in the natural vacuum (space) environment. This paper addresses the thermal degradation of some polymer materials typically used as electrical insulation in partial vacuum. Pyrolysis data for various polymers, from the literature, is discussed. The results of a survey of published pyrolysis data, which identifies the primary gaseous decomposition species for such materials, is presented. The importance of identifying these by-products as they relate to microscopic volume breakdowns and partial discharges is highlighted.

Introduction

Polymer materials in an aerospace (partial vacuum) environment, widely used as both electrical and thermal insulation, as well as vehicle structure, will outgas with time due to various surface desorption and decomposition mechanisms. These gases can remain trapped for long periods of time within spaces such as those existing between insulation laminations or voids within the insulation bulk. Nevertheless, the use of polymers as insulation in electrical power components is a fact of life that can simply not be avoided and must be dealt with on an engineering level. One way this is being done is by the development of organic materials (polymers) which are less subject to decomposition at high temperatures. But there are a lot of polymer materials currently in use in airborne and spacecraft electrical insulation systems, and more will be put in service with such materials in the future.

Polymer Material Degradation

Degradation of polymers can be classified in different ways. Classification is usually based on the dominant features with regard to the causality of the deterioration or the response of the polymer on the molecular level. From an engineering viewpoint, the former method is more relevant, particularly if the main considerations are with respect to macroscopic material properties and localized environmental effects. In each case, some external mechanism usually contributes energy to the molecular structure of the polymer which dissociates the intermolecular bonds in the chain. Within this context the major degradation mechanisms include thermal, radiative (photonic/UV), mechanical (stress), and chemical [1]. Whether or not the degradation occurs in the presence of oxygen can influence the nature and quantity of the gaseous by-products.

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE	2. REPORT TYPE	3. DATES COVERED
JUL 1995	**N/A**	**-**

4. TITLE AND SUBTITLE
A Survey Of Thermal Decomposition Of Solid Insulations And Its Relevance To Breakdown Mechanisms In Partial Vacuum

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Aero Propulsion and Power Directorate Wright Laboratory Wright-Patterson AFB, OH 45433

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release, distribution unlimited

13. SUPPLEMENTARY NOTES
See also ADM002371. 2013 IEEE Pulsed Power Conference, Digest of Technical Papers 1976-2013, and Abstracts of the 2013 IEEE International Conference on Plasma Science. Held in San Francisco, CA on 16-21 June 2013. U.S. Government or Federal Purpose Rights License.

14. ABSTRACT
Several practical issues must be considered when solid electrical insulation is used in a low pressure environment. While the low pressure environment or partial vacuum (in this context, a region which is almost devoid of any gaseous media) can exhibit good electrical insulating properties, the materials contained within the partial vacuum will effect the insulation integrity over time. Degradation of the insulating properties of the partial vacuum may be due to outgassing of enclosed materials and/or adverse media contained in the natural vacuum (space) environment. This paper addresses the thermal degradation of some polymer materials typically used as electrical insulation in partial vacuum. Pyrolysis data for various polymers, from the literature, is discussed. The results of a survey of published pyrolysis data, which identifies the primary gaseous decomposition species for such materials, is presented. The importance of identifying these byproducts as they relate to microscopic volume breakdowns and partial discharges is highlighted.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			
unclassified	**unclassified**	**unclassified**	**SAR**	**6**	

These mechanisms discussed above may not always be associated with influences of the local environment on the polymer. During processing and forming, thermoplastics can experience high degrees of thermal and mechanical stress, which can contribute to deterioration. In the fabrication of insulating films and sheets, microvoids can form inside the material. Logically, these voids can then be expected to be filled with the decomposition gases which evolve at the processing temperatures. This is difficult to confirm analytically in any non-intrusive manner. The importance of these voids in the electrical breakdown mechanism known as partial discharge will be discussed later. It is worth noting that the partial discharge mechanism can repeatedly deposit small amounts of energy (10^{-8} joules) in very short time intervals (10^{-8} sec) resulting in local heating within the voids. Alone, this internal heating can easily raise the surface temperature inside the void to over 200 degrees C [2].

Within the context of utilizing an enclosed compartment for the polymer insulated, high voltage components on board a spacecraft, non-oxidative thermal degradation is the most relevant mechanism. Low energy photonic and ultraviolet radiation should not be a problem inside the space vehicle's outer skin. High energy radiation decomposition mechanisms are difficult to prevent. The same vacuum space which can be utilized for its excellent electrical insulating properties, also provides good thermal insulation. It is easy to see how a component may be subjected to high internal temperatures, due to inherent, parasitic power losses.

Polymer Decomposition Testing

Pyrolysis of polymers is the study of the high temperature degradation of polymer materials under controlled conditions. A prepared sample is typically heated at a constant rate over a specific temperature range, while the material's weight loss and volatile by-products are measured. Most pyrolysis work is related to combustion processes accompanying burning, flame spread, and volatile gas phase reactions. Pyrolysis temperatures are usually as high as 1000 degrees C. In order to attain quantitative, molecular weight spectral data on the gaseous by-products, a combinations of mass spectrometry, gas chromatography and thermogravimetry are generally used.

In the case of polymer insulating material degradation within an enclosed vacuum environment on board a spacecraft, the volatile by-products of interest are likely to be evolved at temperatures much lower than those typical of most pyrolysis testing. The pertinent region is about 200 degrees C above the maximum recommended operating temperature (150-250 degrees C) for the particular material. Above this, the characteristic electrical properties of the polymer insulation begin to degrade. It is assumed that extended operation with hot spot temperatures above these limits would degrade component performance, resulting in catastrophic internal failure. From a breakdown mechanism viewpoint, it is the charge transport and growth properties of the gaseous decomposition products that might be evolved into the vacuum spaces and voids, under typical power component operating temperatures, that is of interest.

Before the electrical transport properties of such gaseous products can be studied, the constituents of the mixtures must be identified. A survey of the literature has been made to evaluate the published pyrolysis data relevant to polymer materials typically used for electrical insulation. Since the application of a polymer material as an electrical insulator is a fairly vast subset, further qualifiers included:

1) Significant usage in current aerospace or spacecraft systems.
2) Good vacuum compatibility, i.e. low outgassing rates under quiescent conditions.
3) Materials which retain their electrical characteristics at high temperatures.
4) Thermoplastics which can easily be machined or formed.
5) Epoxies or multi-part composites, whose properties can change drastically, depending upon formulation, processing and curing, have intentionally been omitted.

Specific attention was paid to pyrolysis products which evolved from the materials at relatively low temperatures, i. e. less than 600 degrees C.

The pyrolysis data found in the literature search has been summarized in Table I. The table displays the volatile gases found in primarily non-oxidative pyrolysis tests of various polymer

Table I. Decomposition Products of Polymer Materials

MATERIAL	CO_2	CO	H_2O	HCN	SO_2	H_2	NH_3	CH_4	Toluene	Benzene
Polyimides:										
Kapton H [4, 5, 13, 14]	x	x		x						
Kerimid [5, 15]	x	x	x							
PM Film [16]	x	x	x							
Skybond 700 [3]	x	x	x	x		x	x	x		x
Polypropylene [6]										x
Polysulfone [6, 7, 8]	x		x		x	x		x	x	
Polycarbonate [9]	x	x						x		
Nylon [10]	x	x (some types)	x				x			x
Poly-p-oxybenzolate (like Teflon) [11]	x	x								
Polybenzobisoxazole-phenylene (PBO) [12]	x	x	x	x						
Ethylene-propylene-diene (EPDM) [17]	x	x						x		

materials, as indicated by the "x". In addition to the more common groups, data is included for a relatively new dielectric film (PBO) and a ductile, rubber compound (EPDM) utilized in applications requiring flexible insulation. These tests were typically performed in a vacuum or inert gas environment. Relative concentrations are not included, since they are dependent upon such variables as: measurement technique, instrumentation sensitivity, carrier medium utilized (inert gas or vacuum), etc..

It can be seen from Table I that certain molecular gases frequently appear in the pyrolysis tests, as a constituent decomposition product of the polymer material groups listed. Both CO_2, and CO are frequently present in significant concentrations. In particular, CO_2, CO,

H_2O, HCN, and benzene are in evidence. While it is true that the presence and amount of H_2O detected can depend upon the sample preparation, polyimides, for example, do form H_2O when their molecular chains break-up [3]. This was verified experimentally by Crossland and associates [15], who pyrolyzed Kerimid samples at successively higher temperatures, always seeing H_2O as a by-product from the sample.

Within the context of the insulation requirements on board a spacecraft, as previously mentioned, it is the lower degradation temperatures that are most relevant. The volatile decomposition products change with increasing temperature. For example, this can be seen in the published pyrolysis data shown in Figure 1 [3], which is for a polyimide material (Skybond 700). The primary decomposition by-products below 450 degrees C are CO and CO_2.

It should be noted that time periods during which pyrolysis data is taken are typically tens of minutes to hours, due to slow sample warming rates and measurement constraints. Slow pyrolysis data may be more relevant to insulation in components energized continuously or with long duty cycles. Those operated in a burst mode are less likely to follow the thermal decomposition sequence and more probably be dominated by conventional outgassing products.

Microscopic Volume Breakdown

The phenomena of partial discharges is directly related to the electrical breakdown of a gaseous insulated volume, on a very small scale. Usually microvoids or enclosed, gas filled spaces are formed unintentionally in solid dielectric insulation during manufacture or processing. Due to the differences in relative dielectric constant between typical solid insulation and gas, a significant percentage of an externally applied ac (or fast transient) electric field can be impressed across an internal void. If this local field is greater than the breakdown strength across the gap, a charge transport, known as a partial discharge will occur. The magnitude of the applied electric field at which partial discharges first start to occur is way below that required to cause a bulk breakdown within the solid insulation. Hence the corona inception voltage (i.e. the applied voltage at component terminals for which partial discharge activity is externally detectable) will depend upon the gas species contained in the voids.

The partial discharge phenomena can be dominated by different mechanisms depending on the surface resistivity of the initiating electrodes and the uniformity of the field across the void. The charge transport mechanism can be broadly categorized as either Townsend-like, with primary ionization coefficient and secondary feedback mechanisms, or streamer-like, referring to a single avalanche that reaches a critical number of electrons (typically 1×10^8). In practice, many partial discharges within insulation voids are Townsend-like in nature [2]. Devins [18] derived an expression for the current flowing in the external circuit due to a Townsend-like discharge within an ideal void inside a capacitive element as

$$I(t) = \frac{w_d\, q_0}{\Delta} \exp(\alpha w_d t)$$

where $\Delta = \delta\,\{(1 + \delta')/\varepsilon\delta'\}$ and δ and δ' are the respective thicknesses of the void and solid dielectric material, and q_0 is the initial electronic charge. The two charge transport parameters, drift velocity (w_d) and ionization coefficient (α), are explicit in this expression.

Charge Transport in Gas Mixtures

Table I brings up an interesting aspect of thermal polymer degradation. While certain components may dominate the decomposition process, other components are typically present

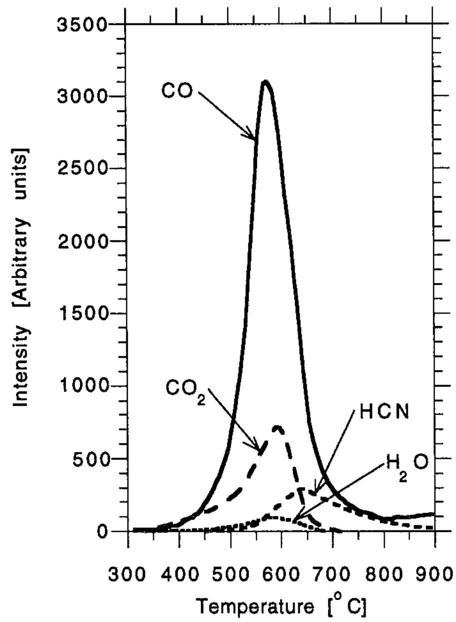

Fig. 1 Typical Pyrolysis Data for Polyimide in Vacuum [3]

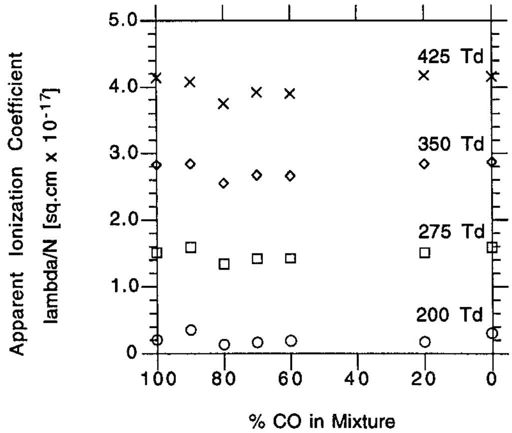

Fig. 2 Apparent Ionization Coefficients for CO, N_2O and Mixtures

in small quantities. As an initial estimate, the charge transport properties and breakdown potentials of a gas mixture can be scaled by partial-pressure-weighting. In certain specific cases, this is true, but it certainly is not true in general [19]. Small amounts of certain gases can have a significant effect on the electron/ion transport properties of the gas mixture. This is particularly true if the trace gas is highly electronegative.

For example, Figure 2 [20] shows apparent ionization coefficient measurements made on mixtures of CO/N_2O for various values of E/N, expressed in units of Townsends (Td; 1 Td = 1×10^{-17} V-cm^2). From 275 to 425 Td, there is a decreasing trend in the coefficient for a range of binary mixtures containing from 60 to 90% CO. At 425 Td, the coefficient value is 10% below that of the pure gas components, indicating an effective increase in the dielectric withstand strength of the gas mixture compared to either pure gas.

Conclusions

An analysis of the information contained in Table I and Figure 1, would seem to indicate that mixtures of CO_2 and CO are the most generally relevant to electrical insulation in an enclosed vacuum environment. While H_2O is also a real decomposition product inherent in the breaking of certain polymeric bonds, the quantity of H_2O detected is dependent upon the sample preparation. This is evidenced by variations in the quantity of H_2O detected in different sets of pyrolysis data for essentially the same polymer [10]. It is emphasized that the thermal degradation process of the solid insulation can aid or degrade the dielectric withstand strength of the enclosed volume, and hence affect the corona inception voltage. Measurements of the charge transport and growth parameters for individual binary mixtures of decomposition gas species (CO_2, CO and N_2O) have been reported on earlier [20 to 22], and they provide important information for predicting breakdown phenomena in such environments.

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